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XVIII.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY.

WAVE-LENGTHS OF METALLIC SPECTRA IN THE ULTRA VIOLET.

By John Trowbridge and W. C. Sabine.

Presented March 14, 1888.

PART I.

Introduction.

The Catalogue of Metallic Spectra, revised by a Committee of the British Association, and published in its volumes for 1885 and 1887, is an extremely valuable contribution to the subject of spectrum analysis; it contains the material for future generalization in regard to the molecular structure of so-called elements, or in regard to the harmonic relations which may exist between their wave-lengths. Here can be found in juxtaposition the results of various observers upon the metallic spectra of the same metal, and the student can judge of the relative accuracy of the results. A superficial inspection of this Catalogue will show that even distinguished observers, like Thalen and Kirchhoff, often differ in their results by one part in 4,000, or one part in 2,500. No observer of metallic spectra gives results to more than one tenth of Angstrom's unit, or to more than one tenth of one wave-length. Physical science, however, now demands a greater degree of accuracy. Various hypotheses in regard to the apparent coincidences between lines of metallic spectra and lines in the solar spectrum have been propounded, and can only be settled by more accurate measurements of wave-lengths. There are also questions constantly arising in regard to the displacement of lines of spectra due to the motion of the stars and to changes of temperature, which require a greater degree of accuracy in the measurement of wave-lengths of gaseous and metallic spectra than the results of previous observers afford. It may be remarked, that observations upon the metallic spectra of metals from the limits of the visible red to the limits of the visible violet have become comparatively easy; for the solar spectrum can be used to identify the lines of the metals, and to ascertain their wave-lengths. It is only in the extreme infra red region and in the ultra violet that such observations become difficult. In these regions we must trust to photography to reproduce by long exposures of the sensitive plate the feeble lines of metals which may manifest themselves there. In the infra red region, as far as wave-length 10,000, it is possible to photograph the solar lines, and we can compare the spectra of such metallic lines as may exist between the A line and the limit 10,000 with the solar spectrum. Beyond this limit, and beyond wave-length 2800 in the violet, the solar spectrum disappears, and the problem of measuring the wave-length of metallic lines which extend beyond these limits becomes a difficult one.

Besides the resolution of the difficulty of measuring the wave-lengths of the invisible rays of light with proper accuracy, the measurement of such wave-lengths is destined to prove a crucial test for various theories which must arise in the progress of physical science. The lines of the metals are exceedingly numerous in the ultra violet region, far more so than in the infra red region. If there are any harmonic relations between the wave-lengths of the spectra of metals, it is here that one might expect to observe such relations. Indeed, Professor Grünwald of Prague has lately enunciated a remarkable hypothesis upon the relations between the wave-lengths of so-called elements, and finds in the observations of various observers in the ultra violet a strong confirmation of his hypothesis. In any theoretical work upon the grouping of spectral lines, it is of fundamental importance that the wave-lengths of the lines should be determined with as great accuracy as possible. The coincidence of metallic lines with solar lines is at the best a doubtful piece of evidence. This evidence is of moment only when the number of coincidences becomes great, and is accompanied by characteristic grouping. A mistake of a wave-length in the question of position is sufficient to destroy the support which the author of any hypothesis might claim for it.

Conditions for Accuracy of Measurement.

All measurements of wave-lengths hitherto published have been made by the old method of angular measurements with a spectrometer. We say old, for the use of Rowland's concave grating with its peculiar mounting must be characterized as a new method and a new departure in measurements of wave-lengths. The observation of wave-lengths of metallic spectra by the eye is most laborious, and the photographic plate must be substituted for the eye for most purposes. The angular positions of the spectral lines on such a plate assume great importance, for upon these positions depend the value of the wave-lengths. In the operation of photographing spectral lines, it is necessary to substitute, for the observing telescope and micrometer eyepiece of the spectrometer, a camera box provided with a suitable lens, and with a plate holder for the photographic plate. Unless the latter is small, the spectrum will not be in focus on all parts of the plate; moreover, unless the distance of the photographic plate from the diffraction grating employed is comparatively large, the distances between the spectral lines on the photograph will not be proportional to wave-lengths. To determine these wave-lengths recourse must be had to various devices. The one usually employed is due to Cornu, and can be found described in the Annales de l'École Normale, 2 série, tom. iii. p. 421; also in Journal de Physique, X., 1881, p. 425. It consists in photographing images of the slit of the spectroscope upon the photographic plate, by turning the graduated circle of the spectrometer through measured angles. These photographic images serve as fiducial marks, by means of which wave-lengths of spectral lines on the plate can be calculated. In the case of diffraction spectra obtained by deflecting a bundle of parallel rays at the angle of incidence, i, with a deviation of order n, Δ_n is connected to the wave-length λ, and with a certain constant, a, of the grating by the formula

$$2\,a \sin \frac{\Delta n}{2} \cos \left(i - \frac{\Delta n}{2}\right) = n\,\lambda.$$

It is evident that at least two errors can arise in the use of this formula; one from defective graduation of the circle of the spectrometer; another from the process of referring from the photographs of the slit on the plate to the photographs of the metallic lines.

We select the work of Hartley and Adeney* as perhaps the best type of this method of using a camera with a spectrometer. Their work is characterized by great care and thoroughness, and no one could probably attain better results by the use of a flat grating, with its concomitants of collimator, photographing lens, and camera. These observers state that they were not troubled by the underlying spectrum of a higher order than that which they photographed, for it was not brought to a focus with the latter. In the new method we propose to illustrate, all the spectra are in focus together, and this fact, instead of being an obstacle, can be turned to great advantage. In the absolute measurements of the wave-length of light, the spectrometer method with eye observation and with a micrometer is unquestionably more accurate than any photographic method. We have in this determination to deal with comparatively large quantities, and with well defined directions, which can be made to coincide with optical axes of the instrument; this is not the case, however, with the majority of the spectral lines on a photographic plate placed in a camera, which replaces the observing telescope of the spectrometer. The photograph contains possible errors, and any shifting or movement of the spectrometer circle to determine intervals on the photographic plate is apt to introduce other errors.

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* Philosophical Transactions, CLXXV., 1884, pp. 63–137.

The ideal arrangement would seem, therefore, to be a photographic apparatus which should remain in focus for all the spectra of the different orders, in which distances between successive lines on the photographs of the spectra should be closely proportional to wave-lengths, so that, the constant being known for a certain position of the sensitive plate, the wave-lengths can be determined by simple linear measurement. Moreover, it is desirable, as we have said, that the underlying spectra should be brought to the same focus as the overlying; for by this means we can compare the wave-lengths of lines in the spectra of different orders, and halve our errors. It is true that some confusion results from having the metallic lines in the spectra of different orders photographed upon the same plate ; but a little experience enables one to separate the lines with comparative ease, and the gain in accuracy compensates for the additional trouble.

The apparatus which best answers the requisitions we have pointed out is that of the concave grating of Rowland, with its peculiar mounting, which has been fully described in the American Journal of Science, Vol. XXVI., 1883, p. 87.

Objects of the Present Investigation.

The conclusion of the work of the Committee of the British Association on the tabulation of metallic spectra seemed to us to require a survey of the work, which must be done in the future in order to perfect and correct the work of the past. We have therefore examined the tables given by the committee in order to see what lacunæ could be supplied, and to point out the directions for routine work which may afford material for future generalizations. In the pursuance of this work, we have been compelled to examine the accuracy of measurements of wave-lengths hitherto made in the ultra violet. With the aid of the new Map of the Solar Spectrum published by Professor Rowland, it is very easy to determine the wave-length of metallic lines in the visible spectra of metals; for it is merely necessary to photograph a portion of the solar spectrum upon the same plate as that which receives the spectra of the metals under consideration, and then to refer to the published map. We have already remarked, that even a superficial examination of hitherto published catalogues of wave-lengths of metallic spectra will show that distinguished observers differ in their determinations by one or two wave-lengths. The task of remeasuring the wave-lengths of metallic lines is a very great one, and approaches in character the routine work now prosecuted in astronomical observatories in the redetermination of star places, the photometric intensities of stars, and the classification of star spectra. In our present work we have confined our attention to ultra violet spectra. Since the solar spectrum disappears in the neighborhood of wave-length 2800, the task of identification of wave-lengths becomes a very serious one. To replace the solar spectrum we must refer the lines of metallic spectra to carefully measured lines of certain metals. When one metal ceases to give spectral lines, another must be selected. To test the relative accuracy of what we have termed the old method of measurement with that of the new, we have measured the lines of electrolytic copper, and have compared our results with those of previous observers in regard to the distribution of errors. Besides the comparison of accuracy, we have examined the limit of the spectra of copper in the ultra violet, in order to see if that given by previous observers could be extended.

Apparatus.

The apparatus consisted of a concave grating of 21 ft. 6 in. radius, mounted in the manner described by Professor Rowland. The camera was provided with a shutter, which enabled us to expose different portions of the sensitive plate at pleasure. An alterating dynamo machine was employed, together with a Ruhmkorf coil. The alterating machine gave from eight to ten thousand reversals per second. With a battery of from six to ten two-quart Leyden jars, a powerful spark was obtained between the metallic terminals which we employed. The spark was produced close to the slit of the apparatus, and the time of exposure varied from one to two hours. At various times endeavors were made to substitute the more powerful light of the carbon electric light for the electric spark, in the hope of shortening the time of exposure; but these efforts were not successful. If they had been, we should have been obliged to struggle with the question of impurities in the carbons. An exposure of fifteen minutes to the ultra violet spectra of metals burned in the electric light produced no image below wave-length 3000. A quartz condensing lens was employed with the arc light, and therefore no light was lost by selective absorption. With the spark no lens was necessary.

By curving the photographic plate all parts of it remain in focus, and distances on the plate are closely proportioned to wave-lengths. Calling $Y =$ wave-length, we have $Y = C + a\,x$, where C and a are constants, and x is the distance along the plate.

The determination of the wave-lengths of lines extending over a range of three hundred tenth meters involved the taking of three negatives. The sensitive dry plate (2 × 10 inches) was pressed by springs against the "forms" of the plate-holder into an arc of a circle. Having placed the plate-holder on the camera box, the girder bearing the camera and grating was moved along its tracks until the position of the pointer of the carriage on the scale beside the track indicated that light of wave-lengths 4200 to 4800 in the first spectrum and 2100 to 2400 in the second spectrum would fall on the plate. The shutter was turned so as to expose only the lower half of the plate and a photograph of the solar spectrum from 4200 to 4800 taken. The shutter was again turned, and the upper half of the plate given a long exposure to the light of the spark. Both spectra were in focus. The wave-lengths of the metal lines were then found directly, by interpolation on the normal spectrum, from the solar lines whose values were given in Rowland's Photographic Map and table of wave-lengths.* The interpolation was made by means of measurements on a dividing engine. In order to correct for any displacement due to the motion of the spark from side to side, or to jarring arising from the great noise of the spark, and also in order to sift out the lines belonging to the first spectrum from those belonging to the second, the girder was moved to the violet of the third, with its magnified dispersion and different underlying spectra. The metal and solar lines were taken side by side, and the interpolation for the wave-lengths of the metal lines made as before. From this the correction to be applied to the previous plate was found, amounting in some cases to .2 of a tenth meter. The correction thus found was applied to all of the lines on the plate. The girder was now moved so that the sensitive plate was in the extreme ultra violet of the first spectrum, and the plate exposed to the light from the spark. From this negative the value of the wave-lengths of the faint lines were obtained by interpolation from the values of the stronger lines as determined by the first plate. It also served as the final test whether the lines on the first negative were of the first or second order. All of the lines more refrangible than line 2123.1 were in the case of copper found from this negative and from line 2136.1 by direct measurement.

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* American Journal of Science, March, 1887.

Another method of distinguishing which lines on the first negative belong to the second and which to the first spectrum, is to place in front of the slit while taking the metal lines a piece of plane glass. The second spectrum for this refrangibility will be completely cut out, and only the metal lines of the first remain, being in the visible violet.

The only source of error was in the setting of the microscope upon the broad or faint lines. The probable error of this is about .1 tenth meter. For the few most refrangible lines it may be greater.

Effect of Change of Temperature of Source of Light on Constancy of Position of Metallic Lines.

In the process of the investigation we were much troubled by a slight shifting in position of the metallic lines upon the photographs. This shifting could be observed when the metallic lines were compared with a solar spectrum taken upon the same plate. The amount of this shifting in no case amounted to more than .1 or .2 of a wave-length. At first we thought it might be possible that there was a change in refrangibility of the metallic lines due to a difference in temperature of the source of light, and a long study was made of the influence of the temperature of the source of light upon its wave-length. When a metal was burned in the carbon electric light with varying strength of current, no displacement could be observed between the lines of the metal photographed beneath each other upon the same sensitive plate. When the electric spark with a large battery of Leyden jars was substituted for the electric arc, and the metallic lines obtained by the light of the spark were compared with those from the arc, occasionally a small displacement could be observed. This did not seem to arise from a change of position of the source of light, or from the heating of the slit of the spectroscope. A careful study of the iron lines showed us that the wave-length of the iron lines in the sun and those obtained from burning iron in the electric arc were the same to certainly one hundredth of a wave-length. The displacement we observed was noticed only when the electric spark was employed. This shifting did not arise from a change of position of the spark in our apparatus, for it could not be produced at will by changing the position of the source of light. Moreover, when the arc light was placed in the same position that the spark occupied, no displacement could be observed in photographs taken by the aid of the arc. We were forced to conclude that through the range of temperature afforded by the electric arc and the electric spark the wave-lengths of the metallic lines were constant. The displacement we observed was therefore referred to a jarring of the apparatus due to the noise of the electric spark. When the camera was at a considerable distance from the slit of the spectroscope, the displacement was diminished, and sometimes entirely disappeared. The entire apparatus was very solid, and the camera was clamped to a massive girder. It was difficult, therefore, to believe that the displacement could arise from the noise of the spark. We believe, however, that it can be ascribed to this cause, and that the wave-lengths of metallic lines produced by burning metals in the electric arc or by vaporization in the electric spark are to one hundredth of a wave-length the same as those of the corresponding lines in the sun.

Results.

In the following table we have adopted the same symbols and letters to designate the character of the lines which the Committee of the British Association have employed. Column 1 refers to the intensity on a scale of 10. Column 2 gives our measures of the wave-lengths of the copper lines in the ultra violet, from wave-length 2369.9 to 1944.1. Column 3 contains the measures of these lines by Hartley and Adeney. Column 4 are the corrections to be applied to Hartley and Adeney's results. Column 5 contains measurements by Liveing and Dewar. Column 6, corrections to be applied to their results. Column 7 gives the symbols adopted by the Committee of the British Association, which serve to describe the character of the line.

1. Intensity.	2. Wave-lengths of copper lines. Spark.	3. Hartley and Adeney.	4. Corrections.	5. Living and Dewar. Arc.	6. Corrections.	7. Intensity. B. A.
9	2369.9	2370.1	— .2	....	..	9 br
1	2368.8	2368.7	+ .1	....	..	2 sd
..	....	2365.8	..	....	..	1
4	2356.7	2357.2	— .5	....	..	5 sd
3	2355.2	2355.0	+ .2	....	..	2 sd
3	2348.8	2348.8	0	....	..	2 sd
1	2346.2	2346.2	0	....	..	2 sd
3	2336.3	2336.6	— .3	....	..	3 sd
..	....	2303.8	..	....	..	1 sd
1	2299.6	2300.5	— .9	....	..	1 sd
..	....	2297.5	..	....	..	1 sd
7	2294.4	2295.0	— .6	2294.1	+.3	6 sd
1	2293.9	2294.6	— .7	....	..	3 sd
3	2291.1	2291.4	— .3	....	..	3 sd
3	2286.7	2286.7	0	....	..	3 sd
2	2278.4	2279.6	—1.2	....	..	2 sd
6	2276.3	2277.0	— .7	2276.0	+.3	6 sd
2	2265.5	2265.8	— .3	....	..	2 sd
2	2263.9	2263.9	0	2263.6	+.3	3 nd
2	2263.2	2263.2	0	....	..	3 nd
2	2255.1	2257.7	—1.6	....	..	2 sd
2	2249.0	2250.0	—1.0	....	..	2 sd
7	2247.0	2248.2	—1.2	2246.6	+.4	9 sd
..	....	2247.7	..	....	..	3 nd
7	2242.7	2244.0	—1.3	2242.2	+.5	9 sd
..	....	2243.5	..	....	..	3 nd
1	2231.7	2233.0	—1.3	....	..	3 sd
1	2231.0	2332.2	—1.2	....	..	3 sd
3	2230.1	2231.2	—1.1	2229.6	+.5	5 sd
3	2228.9	2230.0	—1.1	2228.3	+.6	5 sd
2	2227.8	2229.1	—1.3	....	..	3 sd
1	2226.9	2228 1	—1.2	....	..	3 sd
1	2225.7	2227.0	—1.3	....	..	1 sd
1	2224.8	2226 0	—1.2	....	..	1 sd
6	2218.2	2219.3	—1.1	2217.5	+.7	6 sd
..	....	2218 5	..	....	..	3 nd
2	2215.3	2216.5	—1.2	....	..	3 nd
1	2214.4	2215.8	—1.4	....	..	3 sd
2	2213.0	2214.1	—1.1	....	..	2 sd
6	2210.3	2211.3	—1.0	2209.7	+.6	6 sd
..	....	2210.8	..	....	..	3 nd
..	....	2208.8	..	....	..	2 sd
2	2200.6	2200.3	+ .3	....	..	3 sd
3	2199.8	2199.8	0	2199.2	+.6	1 nd
3	2196.9	2196.5	+ .4	....	..	3 sd
4	2192.4	2192.0	+ .4	2191.8	+.6	6 sd
..	....	2191.2	..	....	..	3 nd
4	2189.9	2189.6	+ .3	2189.2	+.7	6 sd
..	....	2188.5	..	....	..	3 nd
1	2181.8	2181.0	+ .8	....	..	1 sd
4	2179.5	2179.0	+ .5	2178.8	+.7	5 sd
..	....	2178.0	..	....	..	3 nd
3	2175.2	2174.5	+ .7	....	..	3 sd

1. Intensity.	2. Wave-lengths of copper lines. Spark.	3. Hartley and Adeney.	4. Corrections.	5. Liveing and Dewar. Arc.	6. Corrections.	7. Intensity. B. A.
3	2149.2	2148.8	+ .4	2148.9	+.3	3 sd
4	2136.1	2135.8	+ .3	2135.7	+.4	3 sd
3	2134.6	2134.2	+ .4	....	..	2 nd
3	2126.2	2124.4	+1.8	....	..	3 sd
3	2125.3	2124.0	+1.3	....	..	2 nd
3	2123.1	2122.1	+1.0	....	..	3 sd
..	....	2121.5	..	....	..	2 nd
3	2117.5	2116.0	+1.5	....	..	1 sd
3	2112.2	2110.5	+1.7	....	..	1 sd
3	2104.9	2103.0	+1.9	....	..	1 sd
2	2098.6					
1	2093.9					
2	2088.1					
2	2085.5					
2	2078.8					
1	2067.0					
1	2062.7					
2	2055.1					
2	2045.0					
2	2037.3					
2	2036.0					
1	2030.9					
2	2025.7					
1	2016.9					
1	2015.8					
1	2013.2					
2	1999.9					
2	1989.4					
2	1979.4					
1	1970.4					
1	1944.1					

Conclusions.

It will be observed that the corrections to be applied to the wave-lengths obtained by Liveing and Dewar are progressive in their nature when compared with those which must be applied to the results of Hartley and Adeney. The difficulty in identifying lines and determining coincidences by employing the tables of metallic spectra in the ultra violet, published by the British Association, is illustrated by our work; for certain lines measured by Liveing and Dewar, which are identified by the committee with lines given by Hartley and Adeney, are in reality removed from each other, one or two lines intervening. In certain cases the lines of Liveing and Dewar are wholly beyond identification with those given by Hartley and Adeney.

The results of our inquiry into the accuracy of the results of previous observers in measuring wave-lengths of metallic spectra in the ultra violet can be summed up as follows.

1. We believe that the method of photographing images of the slit upon the photographic plate, due to Cornu, in order to determine positions, leads to unavoidable errors.

2. The best method of determining wave-lengths of metallic spectra is by the use of concave gratings; for linear measurements are substituted for angular ones; underlying spectra are brought to the same focus as overlying spectra; and, since a great number of lines are in focus on the same plate, the conditions are the same for all, viz. breadth of slit, length of exposure, and source of light.

3. Hypotheses in regard to coincidences of gaseous and metallic spectra cannot be safely based upon existing measurements of spectra in the ultra violet.

4. The limit of the copper lines is extended by our investigation.